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THE COMPLEX BAND SPECTRUM OF COLUMBIUM OXIDE (THE DIATOMIC MOLECULE CbO)

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Plates IA, B, C

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ABSTRACT. An extensive band system attributable to the diatomic molecule CbO is obtained in the region from λ 4200 to the limit of sensitivity of the panchromatic plates. The bands are divided into three systems, *A*, *B*, *C*, analogous to the α, β, γ-systems in TiO and ZrO, found by Lowater The following vibrational constants are determined for the three systems :—

	ν_e	ω_e'	$x_e'\omega_e'$	ω_e''	$x_e''\omega$
System *A*	21400	855.2	3.9	1002.9	6.5
System *B*	(18280)	998	16	1000	6.5
System *C*	(16260)	992	7.5	1000	6.5

Evidence of multiplet structure is found and electronic transitions between quartet terms are suggested as probable.

INTRODUCTION

The spectra of the diatomic molecules of the transition group of elements are of particular interest b th theoretically and experimentally. The interest lies in the fact that the elements contain an incomplete '*d*' electron shell and form molecules which give rise to bands of a very complex structure,—in appearance line-like, with a considerable overlap of multiplet and partially resolved rotational structure. These complex features are explained by the identification of high multiplicity terms among the eletronic states for these molecules such as those established in the case of MnH (Nevin 1942, 1945), Mn halides (Muller, 1943; Bacher, 1948, and Rao,' 1948) and CrCl (Rao and Rao, 1949). Another set of examples of bands of this type are those of TiO and ZrO (Lowater 1929, 1932). The multiplicity of terms involved in the emission of this later type of bands may not be "high" but the mechanism of electron configuration and transitions is analogous to the first type of bands. There is further an astrophysical interest associated with these oxide bands, since some of them are conspicuously present in the stellar spectra. The band spectra of the oxides known till now are those of Sc, Ti, V, Cr, Mn, Fe, Co and, Ni in the first transition group and Yt and Zr in the second transition group, but there is no mention or reference till now in the literature to the band

spectrum of the oxide of columbium. While engaged on a study of the lines of Cb the author first observed bands in an arc excited between Cb electrodes, which are of a high degree of spectroscopic purity and are specimens of the H. S. brand supplied by Adam Hilger. Subsequently, in an attempt to obtain the bands of CbCl molecule (a small quantity of the pentachloride was supplied by Johnson and Mathey) in a heavy current discharge, the same bands were observed. These are not coincident with any known bands and are assigned to the oxide molecule of columbium. An investigation on these bands is described in the following pages :—

EXPERIMENTAL

The bands are obtained in three different sources:

1. In the flame of direct arc between columbium electrodes run at 220 volts and 3·amperes

2. In the flame of D.C. arc between graphite electrodes fed by columbium pentachloride.

3. In a heavy current discharge from a D.C two kilo-watt generator with columbium pentachloride in the quartz discharge tube. The excitation in this case may be due to the formation of the oxide as a result of the easy decomposition of the pentachloride.

Photographs are taken on S.R. Panchromatic plates with a Hilger two prism Littrow spectrogrph of very high resolving and light gathering power. Measurements of the plates are made as usual and the columbium lines are eliminated by both observation and comparison with the list due to Humphreys and Meggers (1945).

DESCRIPTION OF THE BANDS

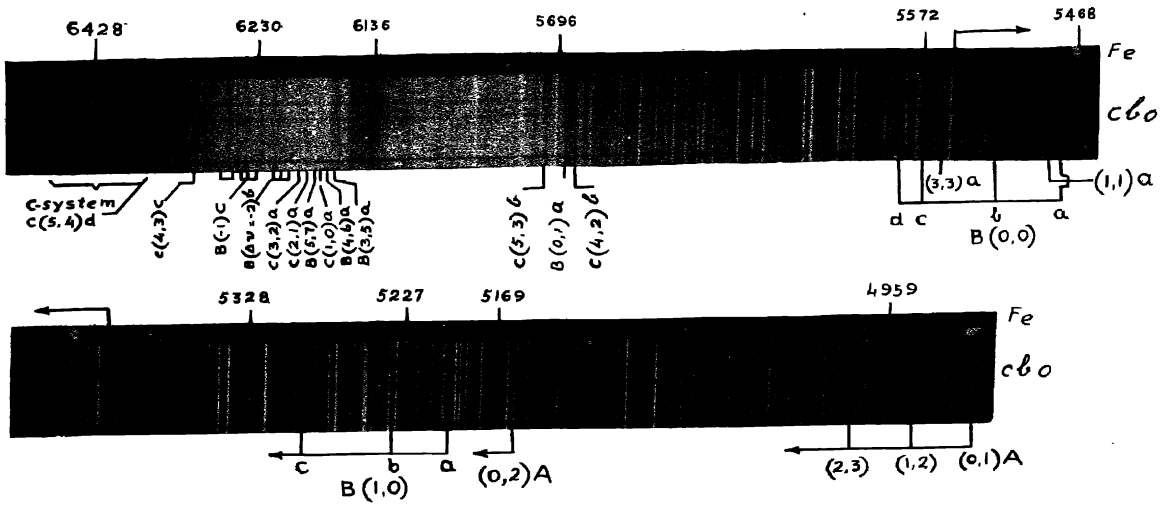
Extensive band systems from λ 4200 to the limit of sensitivity of the Ilford Panchromatic plate are obtained. The bands may be divided into three groups : (Plates IA, B and C).

1. From λ 4200—5100 :—Definite well-marked and red-degraded sequences of which five are conspicuous: we shall designate these as system *A* (after Lowater's system α in ZrO).

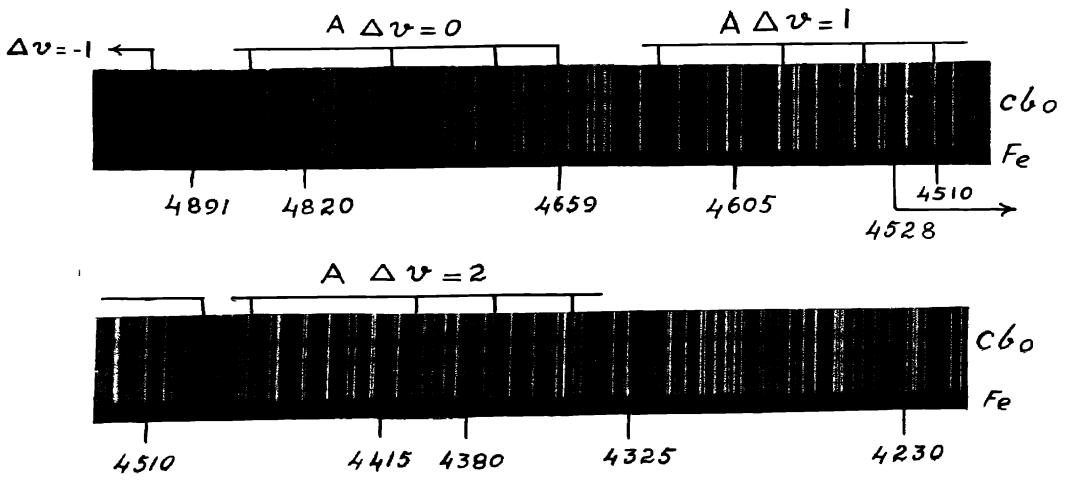
2. From λ 5100—6100 :—Another group of red-degraded bands which does not present any apparent sequence structure. This may be designated as system *B* (corresponding to the β system of ZrO).

3. A third group from λ 6100 to a long wave-length limit which could not be ascertained as the system appears to extend into and beyond the panchromatic region; as can be seen from the photograph. These are closely packed red-degraded bands and shall be considered as a part of system *C* (analogous to ZrO-γ system).

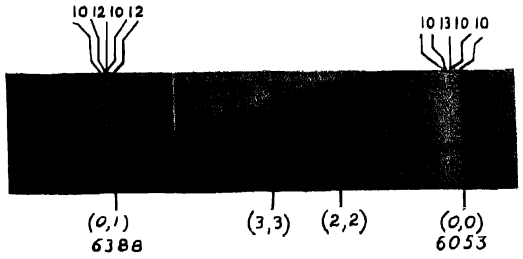
The possibility of the bands forming into three systems is suggested from an examination of the Plates.



Band spectrum of columbium oxide molecule



Columbium oxide bands (contd.).



Chromium oxide bands.

(Glass Littrow)

1. The intensity distribution in each differs from that in any other. There is a comparatively regular distribution of intensity in the sequence-starts of system *A* while the sequences in system *B* are not so conspicuous As we follow the sequences in system *A* there is an abrupt rise in intensity at one stage of the spectrum which suggested the need for considering it as part of another system *B*. An analogous change in intensity characteristics and an apparent discontinuity in the band formation at λ 6100 is very conspicuous on plates with long exposures. It is quite likely that there is an overlap of continuum in this region extending to longer wave-lengths.

2. The structure of the bands also conspicuously differs from group to group and leads to the division into three different systems. There is an apparent partially open rotational structure in system *A*. the structure is much less open in system *B*, and, in system *C* there is no rotational structure at all.

3. Comparison with the other known oxide bands also supports this division into three systems. TiO and ZrO have three systems of analogous bands in the corresponding regions with similar characteristics In the spectrum of vanadium oxide (Mahanti, 1935) though only one system corresponding to system *A* was analysed, mention was made of other bands lying on the long wave-length side of these The VO system has an open rotational structure like that of CbO. Comparison with CrO bands also suggests that the system analysed by Ghosh (1932) probably corresponds to the system *A* in CbO and the α systems in TiO and ZrO. The measurements of Furguson (1932) suggest the possibilty of extensive band systems lying in the infra-red region for CrO and VO molecules.

ANALYSIS

The three systems described above are not isolated ones with wide separations between them : there is a considerable amount of overlap which makes the process of picking out the sequence members a matter of difficulty especially in system *B*. There is, however, a large portion of system *A* in the region of shorter wave-lengths which is comparatively free from overlap. This helped in the easy identification of the structure of the sequences in the system *A*, and hence this is taken up as a starting point of the analysis. The most intense sequence appears at ν 21320 and is likely to be the $\Delta v=0$ sequence. When successive differences between the sequence starts are taken we get, beginning from the violet end the values are 830, 840, 981, 971, 960, etc. It is presumed that 981, 971, 960, are the $\Delta G(v)$ values of one electronic state and 840, 830, etc , of another state. As the bands are conspicuously red-degraded we may expect ω_e' less than ω_e'', and assume that the higher intervals, 981 etc., correspond to the ground state differences. Thus the band heads at ν 21320 and ν 20340 are considered as (0,0) and (0,1) respectively, while that at ν 22163 is taken as the (1,0) head. After fixing up these three bands the (1,1) band is located in the calculated position and is identified as such. With these four bands the analysis of the other bands is developed, as shown in Table I.

TABLE I

Deslanders' Scheme CbO System *A*.

v'' / v'	0	(981 9)	1	(970 2)	2	(964 5)	3 946 9	4	(932 9)	5	(918)	6 901)
0	21320 5(10)		20339 9(6)		19367 6(4)							
(842.0)	(842.7)	(980 7)	(840 1)	(973 3)	(813 3)							
1	22163 3(8)		21180 0(3)		20210 9(4)							
(837 9)	(837 1)	(983 3)	(838 6)	(969 1)								
2	23000.4(3		22018 6(5)				20087 2(5)					
(829.8)		(981 8)	(831 8)				(827 8)					
3			22850.4(2)		21879 5(2)		20915 0(3)		19967 4(1)			18119 3(3)
(818.9)				976 9)	(818 7)	(91 5)		(937 6)				
4					22098 4(4)							
(814 7)					(814 7)							
5					23513 1(5)							
(802.4)									21603 7(4)		20670 8(4)	19752
6									(802 1)	(932 9)		
(795)							23352 3(3)	(946 2)	22406.1(3)			20554 6(1)
7											22269 8(3)	
(792.7)											(792 7)	
8											23062 5(3)	

TABLE II

Vibrational constants of systems corresponding to system *C* in CbO.

Molecule	ω_e'	ω_e''	$x_e'\omega_e'$	$x_e''\omega_e''$
TiO	833.1	1003 5	4 5	5 1
VO	864 8	1012 3	5.7	5.3
CrO	750.7	893.8	8.9	6 5
MnO	792 0	840 7	18.3	4 9
ZrO	820.0	937.2	3 3	3 5
CbO	855 2	1002 9	3 9	6 5

The ground state differences, etc., agree well with the corresponding values of ZrO (Zr being the element preceding Cb in the periodic table). A comprehensive table of the ground and upper state frequencies of the oxide molecules of some of the elements of the transition groups is given above (Table II.) The order of magnitude and the general variation show a regularity and support the correctness of the the identification in CbO

INTENSITY DISTRIBUTION IN SYSTEM A

The most intense heads of the group are the sequence-starts : they fall on a typically wide Conden parabola. Considering any single sequence, the intensity falls rapidly. The fall is very conspicuous in $\Delta v = 0$ sequence But, one peculiarity is the abrupt change in intensity in the $\Delta v = 0$ sequence ; the (2,2) band is not observed at all although higher members of the sequence are developed. In the other sequences as well, some of the earlier members of the sequence are absent while the higher members are sufficiently intense, as is evident from the Table I. Such a general feature is not uncommon in the complex oxide bands; notably in the CrO the (1,1) band is very weak while the (2,2) (3,3) etc., are much stronger.

Another characteristic feature of the intensity distribution deserving particular mention is the relative intensity of the (0,1) and the (1,0) bands. The latter is much more intense than the former, and even comparable with the (0,0) band. This feature also seems to be present in other complex bands as well the oxide bands of Ti, V and Cr and also the halide bands of Mn and Cr.

STRUCTURE OF THE BAND SYSTEM

On account of the above peculiarities in the intensity distribution, considerable difficulty is experienced in arriving at the vibrational structure of the system. Another factor also has contributed to this difficulty. Although each sequence could be generally followed upto the start of

the next sequence, still the following up of each of the sequences after the first two members presented considerable difficulty. It can be seen from the plates and the wave-length list (Table V) that between the (0,0) and (1,1) bands there are at least half a dozen heads with fairly considerable intensity. Whether these bands are rotational heads or multiplet heads could not be decided. Multiplets were detected in the bands of ZrO by Lowater. An attempt to find out similar multiplet structure in the present CbO system *A* is not fruitful. The question of structure (rotational or multiplet) can be considered only after a detailed rotational analysis is obtained. The interpretation of many of the heads which are still unclassified, particularly those at the end of each sequence, might then be clear The intensity characteristics of the bands alone do not give us any clue to their interpretation. Unless the rotational analysis is completed even the question of the existence or otherwise of multiplet structure cannot be decided. Even if the multiplet structure exists, the separations that are involved may be very small, as will be seen from a discussion given subsequently.

SYSTEM B

With the vibrational differences obtained from the structure of system *A* an analysis of system *B* is attempted. The identification of the $\Delta v = 0$ sequence has not been as easy as in system *A*. From analogy with the ZrO molecule we may expect this system to have a common state with system *A* probably the lower state. Attempts are therefore made to see if the ground state differences of system *A* occur in any of the pairs formed from what might be the sequence starts in appropriate regions of system *B*. This resulted in the identification of a number of pairs with the same ground state intervals over short regions of the spectrum. This is in definite contrast to system *A* where no existence of such pairs could be found. A close scrutiny of these pairs and a consideration of the relations between the wave-numbers of this and of the remaining heads, resulted in the vibrational scheme shown in Table III. Under each v', v'' combination four members are given. These are designated as *a*, *b*, *c*, *d* in increasing order of wave-lengths. These members might arise from the multiplicity of the term.

A discussion of the interpretation of these components is given later. It should be noted that all the (v', v'') bands do not develop these four components still their existence and the regularities among them appear quite definite.

The following approximate vibrational constants are derived. The constants in the upper state of system *B* are less than those for the lower state consistent with the red-degraded bands. But the difference between the values is very small.

$\omega_e' \sim 998$ cms^{-1} $\quad x_e'\omega_e' \sim 16$ cms^{-1}

$\omega_e'' \sim 1000$,, $\quad x_e''\omega_e'' \sim 6.5$,,

TABLE III

System *b*

v' \ v''	0	979.3	1	968.9	2	964.9	3	949.8	4	5		6		7	8
	a 18275.4 (4)	998.0	17295.4(4)	(970.4)	16325.0(3)										
	(138.3)		(137.2)		(136.4)										
	b 18137.1 (2)	978.9	17158.2(4)	(969.6)	16188.6(2)										
0	(136.5)		(137.3)		(136.8)										
	c 17940.6 (3)	979.7	16960.9(4)	(969.1)	15991.8(4)										
	(60.5)		(62.6)		(60.0)										
	d 17880.1 (4)	981.8	16898.3(2)	(966.5)	15931.8(3)										
948															
	19222.0(8)	976.3	18245.7(3)				16313.6(1)								
	(133.7)						(137.7)								
	?19083.3(4*bl*)						16175.9(3)								
1	(202.0)						(199.4)								
	18886.3(2)						15976.5(2)								
							(58.5)								
			17852.4(4)	(968.8)	16883.6(3)	965.6	15918.0(1)								
928															
					18069.2				16163.9(5)						
2									(196.4)						
									15967.5						
	19753.1(3)								(163.2)						
915							?16844.0(3)	(939.7)	15904.3						
									17078.2(3)	934.5)	16143.7(3)				
			19950.7(2)								(195.1)				
3			(197.6)				18020.1(2)				15948.6(6)				
			19753.1(3)								(157.4)				
913											15891.2(0)				
							19077.6(3)				17201.9(4)	(931.7)	16270.2(4)		
													16130.6(2)		
4											16801.5(2)	(932.5)	16069.0(2)		
														16256.7(6)	
															15994.6(0)
5															15731.3(1)
6															

TABLE IV

System *C*

v' \ v''	0	081	1	2	961	3	936	4	929	5	6	897	7	8
	16263.7(3) 170 4)													
1	16093.3(3) (220.1)													
	15873.2 3) (82.0)													
970	15791 2(0)		16245 2(5) (168.2)											
			16077.0(2) (216 0)											
2	16844 0(3)	(983.0)	15861.0(0)											
	(87 3)		(83.5)											
938	16756 7(3) ?	(979.2)	15777.5(2)											
				16220 6(4)										
3				(174 1)										
				16046 5(1)										
				15740 3(1)										
				17158 2(4)	(963.0)	16195.2(2)								
				(173.0)		(169.6)								
4				16985.2(3)	(959 6)	16025.6(1)								
				(217.5)		(220 3)								
				16767 7(1)	(962.4)	15805.3(3)								
						(87 1)								
						15718.7(1)								
						16930 9(3)	(936 5)	15904.4(0)						
5								15695.6(2)						
								16898.3(2)	(930.8)	15967.5(2)				
6								16588.0(0)	(927 4)	15661 6(2)				
											16114 2(3)			
											(173.5)			
											15940.7(1)			
7											(222.5)			
											15718.2(1)			
											16801 5(2)	(897 2)	15904.3(2)	
													(220.9)	
													15683.4(1)	
8													(81.5)	
													15601 9(1)	

Intensity Distribution:—The intensity distribution in system *B* is highly complex. There is no systematic variation of the intensity of the different sequences or their individual members. This might be attributed to the partially open rotational structure, multiplicity of the band heads, and overlap of systems *B* and *C*.

SYSTEM C

Only one group is detected definitely in this system (Table IV). It presents a kind of flutted structure. A definite vibrational assignment of a single group like this is not possible. The first attempt was to see if this can be the (0,0) group, in view of its intensity but the intervals between the component heads are not of the expected order of magnitude to justify such an assignment. Intensities, and interval characteristics have suggested on the other hand that it might be the (1,0) sequence. The relatively large intensity of this group does not preclude the assignment as the (1,0) group instead of as the (0,0) group for, in this type of spectra the (1,0) sequence is nearly as intense as the (0,0) group. On the assumption that it might be the (1,0) sequence, evidence is found on the plate of a possible existence of the (2,0) sequence in the appropriate region but it is partially developed and overlapped considerably by bands belonging to system *B*.

Multiple heads are identified in some of the members of the sequence and are designated as *a*, *b*, *c*, *d* similar to those found in system *B*. But it should be noted that the component separations in the two systems are different.

If the above tentative assignment of the observed group as the (1,0) sequence prove to be correct the (0,0) sequence should lie further to the red. An investigation into this region was not possible for want of suitable photographic plates.

TABLE V

List of unclassified bands in CbO

Wave number	Int	Wave number	Int	Wave number	Int
23673.6	3	23528.7	2	23270.5	3
661.7	2	483.6	3	263.7	2
651.3	2	475.8	3	249.5	3
629 3	5	460.1	3	229 1	8
616.7	4	452 5	2	224.7	3
613 7	3	445.4	3	210.3	2
606 3	2	430 4	2	180 2	1
599 8	3	426 7	3	172.8	1
586.2	3	414.7	3	161 8	2
578 1	4	391.4	2	146.4	3
566.4	3	342.6	4	121.6	3
556 7	4	332.6	3		
548 7	5	325 1	4	23075 7	4
540 8	1	303.4	2		

TABLE V (*contd*)

Wave number	Int.	Wave number	Int.	Wave number	Int.
22968.7	2	20948.8	4	18350.5	3
955.1	3	910.7	5	332.9	2
936.6	3	876 1	6	282 4	5
905.7	2	832.9		269 0	3
878.2	2	803 3	3	255 3	2
837.0	2	740 9	4	230 7	5
821.1	2	731 4	3	196.1	3
805 0	2	587.9	4	168 4	4
791.6	3	565.2	2	153 1	2
772.0	3	527 0	2	119.3	3
750.8	2	504 3	1	069.2	3
746 7	2	471 3	2	055.8	3
741 0	2	468.9	3	025.8	2
730 1	3	327.5	2		
678 4	3			17987 3	2
648.2	2	20316.5	5	852.4	4
627.9	3	291 1	1	833.7	4
609.9	3	270 4	2	795 4	3
596.7	3	249 3	1	667 0	3
591.4	2	197 0	3	587.6	3
566.8	3	167.3	2	569 3	2
497 0	5	113 4	1	433.2	2
447.6	3	053.9	4	307.3	1
373.5	4	021.7	4	263.6	3
346 9	2			145.1	3
294.1	4	10975.9	2	011.1	2
208.6	2	914 3	3		
191 9	2	893.4	1	16741.5	1
182 3	1	823.2	2	733.4	2
104.0	4	723 9	2	676.5	1
081.8	5	714.5	3	646 7	2
069.6	2	671 6	2	622.1	2
032.6	4	574 5	1		
		552.6	2	16612 1	2
21949 4	2	428 5	4	601 0	1
926.9	4	384.2	6	564 4	1
911 8	3	351.1	4	526.7	2
893 7	4	346 8	1	493.6	3
870 5	2	323.5	8	475.2	2
		287 5	6	458.0	2
21831.1	3	236.4	2	442.8	1
811 5	6	120 8	5	427.9	1
799.6	3	126 3	5	390.2	2
783.6	3	027.6	3	369 5	1
777.1	2	075 2	2	362.2	1
755 0	4	067.1	2	352.5	1
676 3	6			336.0	2
626.3	6	18985 3	2	232.8	2
583 9	5	970 8	4	207.1	0
574.4	6	943.7	1	069 0	2
546.4	6	907.6	2	053.3	4
528 9	5	874 8	2		
490 5	6	838 7	3	15846 8	4
447.0	6	698 0	0	834.2	1
411 3	3	651.9	1	820 0	1
306.2	2			784.0	0
261 5	4	18571.9	3	764.0	1
252 9	4	568 1	3	731.3	1
225 0	3	567.4	2	706.3	1
217.1	2	511.8	3	671.2	2
163 2	4	480.0	2	651.3	1
080.4	1	473.8	3	628.4	0
024.1	4	433 1	1	587.7	2
011 2	2	366.7	3		

The author, however, desires to suggest that it is a very important investigation as it would lead firstly, to the analysis of system *C*. There is in addition a possibility of deciding the question of the multiplicity of the electronic states involved. The system C' is specially suited for the purpose as it is obviously not complicated by the existence of the rotational structure.

The intensity distribution in this system cannot be discussed in the absence of a complete analysis.

VIBRATIONAL DATA

All the vibrational constants determined for the three systems are collected in Table VI. At least for systems *B* and C the order of magnitude alone should be taken as having been determined in the present work. Accurate formulae are not possible to derive without measurements on higher dispersion In Table VII the values of the energies of dissociation etc., are given for a few allied molecules of the type CbO The data for the oxides of Ti, V, Cr, Mn are taken from Mahanti (1935). For ZrO the values are calculated from Lowater's vibrational constants for system α. The values for CbO are derived from system *A*.

TABLE VI

Vibrational constants in CbO.

System *A*	21400	855.2	3.9	1002.9	6.5
System *B*	(18250)	998	16.0	1030	6.5
System C	16260	992	7.5	1000	6.5

TABLE VII

Heat of dissociation, etc. (from systems corresponding to system *A* in CbO)

	E_{mol}	D'	D''	E_{atom}
ScO	2.5	4.6	7.5	−0.4
TiO	2.4	4.8	6.9	+0.3
VO	2.2	4.2	6.4	0.0
CrO	2.0	1.9	3.3	+0.1
MnO	2.2	1.7	4.4	−0.5
ZrO	2.67	6.2	6.4	+2.47
CbO	2.6	5.7	4.7	+3.6

A few points of interest are :

1. In the horizontal row of molecule ScO, etc., E_{atom} is negligibly small, suggesting the probable dissociation of molecules into two neutral atoms in both the states.

2. In the second transition group (Zr, Cb oxides) E_{atom} is large with the result that the molecules may be expected to dissociate probably into an excited metal atom and neutral oxygen in one of the states (perhaps the upper).

There is thus a similarity in members of the same horizontal row but molecules belonging to different rows exhibit largely differing characteristics, as may be reasonably expected.

ELECTRONIC TRANSITIONS

No definite conclusions about the electronic states of the molecule can be reached without a further investigation of the rotational structure of system *A*, or without a complete development and analysis of system *C*. Still the following observations from the allied molecules may help in forming a general and tentative idea of the transitions involved in the emission of the CbO bands.

In TiO and ZrO the multiplicity of the terms involved is three. The three systems detected in each of these are supposed to arise out of the following transitions.

System α . $^3\Pi - {}^3\Pi$

β* ... $(^3\Sigma) - {}^3\Pi$

γ ... $^3\Sigma - {}^3\Pi$

In dealing with these molecules Lowater suggested the above transitions considering the following points.

1. The total number of electrons in the molecule being even the multiplicity is odd.

2. Christy (1927) in the rotational analysis of TiO (α system) suggested that the multiplicity of the terms is three. The occurrence of multiplets (each member consisting of three components) supports this view of multiplicity.

3. Lowater also referred to a suggestion made by Pearse that there should be a resemblance between the electronic configuration of the molecule of TiO and of the atom of Ca. "Each constituent of the molecule not only retains its own two K- electrons but also has a complete ring of eight L-electrons. If so, for the molecule of TiO, oxygen, gaining two electrons from Ti atom, resembles as a constituent of the molecule inactive neon, while Ti having lost two electrons resembles Ca." Thus,

* In TiO this is due to a singlet transition. But, refer also, Gaydon and Pearse: "Idenification of molecular spectra," page 192.

Ti has the outer configurations $3d^2\ 4s^2$ and oxygen $2s^2 2p^4$.

(perhaps it is the $4s^2$ electrons of Ti that go out to oxygen)

The above view is borne out, as Lowater has shown, from a correspondence between the region of occurrence of the bands of TiO, and the region of the atomic transitions in Ca. In general we get bands in regions corresponding to the atomic transitions in the element iso-electronic with the metallic constituent.

These general considerations may profitably be applied to interpret the electronic transitions in the CbO molecule thus .

Cb atom has the outer most electrons $4d^3\ 5s^2$ and oxygen has $2s^2\ 2p^4$.

(*a*) The total number of electrons is 11: the multiplicity must be even and may be two or four. (Higher multiplicities cannot be possibly expected).

There is experimental evidence, as shown above, of the existence of four components in each (v', v'') member definitely in system *B* and probably also in system *C* There is therefore a greater probability of the multiplicity being four.

(*b*) Applying Pearse's suggestion, if there is a transfer or promotion of two electrons from the Cb atom to oxygen, there remains three electrons in the constituent of the molecule effective in giving rise to molecular terms in CbO The CbO molecule may be considered as resembling in its electronic configuration the atom of yittrium which has $4d^3$ outermost electrons giving rise to quartet terms. Similar quartets may be expected in the CbO bands Comparing also the corresponding regions of transitions in CbO and Yt we obtain a satisfactory ratio as in the case of TiO and Ca obtained by Lowater.

ν_e for system *A* is 21420 cms^{-1}.

In Yt I--$3d^2 4s\ ^1P = 15477$ cms^{-1}.

$3d^2 4p\ ^1P^\circ = 37476$,,

Difference $= 21999$,,

Ratio is $\frac{21999}{21420} = 1.03$

The following transitions might be tentatatively considered for the different band systems observed in CbO.

System *A*: $^1\Pi - {}^1\Pi$

System *B*: $(^1\Sigma) - {}^1\Pi$

System *C*. $^1\Sigma - {}^1\Pi$

Consistent with this scheme of electronic transitions we observed four components in each member in system *C* In system *B* as well similar multiplets are observed, but the separations between them are smaller—a feature which may be expected if the $^1\Sigma$ involved in the emission of

system *B* has a small splitting In system *A* however, the question of mulitplet structure as shown in an earlier section is complicated by the existence of rotational structure. The multiplicity corresponding to the ground $^1\Pi$ state has not been detected in system *A*. There is no evidence of recurring frequency intervals that are found in systems *B* and *C*. Perhaps the effective separations are reduced to zero by the very near equality of the intervals in the intervals in the upper and lower Π states. It is necessary to investigate the rotational structure of system *A* in detail before the above view can be established.

COMPARISON WITH SIMILAR MOLECULES

O_2^+ and VO are like CbO, eleven electron systems sand may be expected to give similar electronic states. In O_2^+ the transition was established by Nevin (1938) from a study of the rotational analysis as $^4\Sigma - {}^4\Pi$ and there was good correlation between Budo's calculations (1937) of the rotational characteristics expected for such a transition In VO, however, Mahanti (1935) analysing the rotational structure in one system suggested a transition $^2\Delta - {}^2\Delta$. The absence of Ω-type of doubling even at high rotational quantum numbers seem to to have led Mahanti to exclude the possibility of a ground Π state and the presence of a short and strong *Q* branch ruled out a Σ ground state Still, as Mahanti himself has stated, the criteria of missing lines and intensity relations between the branches for low rotational quantum numbers could not be used to settle the question definitely. If a similarity of electronic transitions can be predicted from the resemblance between the electronic configurations of O_2^+ and VO, it would be more probable to assume a $^4\Pi$ as the ground state The transition of the system may be a $^4\Pi - {}^4\Pi$. A more complete evidence for determining these electronic transitions would be available only if the VO bands are photographed further in the red than Mahanti has done. Mahanti has also indicated the probable existence of such bands in the infrared region.

Chromium Oxide Bands.—The chromium oxide molecule gives band systems having a similar complex structure From a partial vibrational analysis Ghosh (1932) suggested the probability of transitions between singlet or triplet terms. Observations of his pictures and also those obtained by the author and reproduced in the Plate I C, reveal four component heads following each band at the sequence start *i.e.* five component heads in all are observed, associated with each of the sequences starts. Arguing from the analogy and studying the variation of the multiplicities in a row of molecules such as TiO, VO and CrO it would appear that quintet terms are involved in the transition giving rise to CrO bands. Probably a $^5\Pi - {}^5\Pi$ transition may be occurring. A study of the detailed rotational structure of this and the other molecules in the transition groups is very desirable and would lead to an understanding of this subject of electronic states in such molecules.

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